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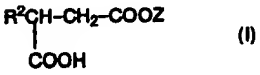
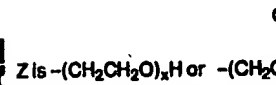
(54) Anionic surface active agents and the preparation thereof.

(57) Anionic surface active agents of the general formula I



(I)

where R^2 is C_{8-12} alkyl or alkenyl; and



Z is $-(CH_2CH_2O)_xH$ or $-(CH_2CHO)_xH$,

where x is an integer of 3 to 35, and the salts thereof with inorganic or organic bases.

These surfactants have excellent surface active properties and hard water tolerance, and may be prepared by conventional esterification techniques.

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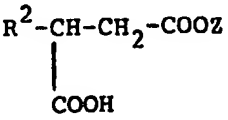
ANIONIC SURFACE ACTIVE AGENTS AND THE PREPARATION THEREOF

This invention relates to anionic surface active agents containing a secondary carboxyl group, and their production.

As is known, anionic surfactants containing a carboxyl group have only limited applicability in hard water. Their calcium and magnesium salts are mostly water insoluble and precipitate out from aqueous solutions. Simultaneously, their surface active properties also change, leading, for example in the case of suspensions or emulsions, to the collapse of the system.

We have found that hemiester derivatives of succinic acid of the general formula I



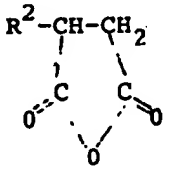
(I)

where R^2 is C_8-C_{12} alkyl or alkenyl; and

Z is $-(CH_2CH_2O)_x-H$ or $-(CH_2\overset{CH_3}{\overset{|}{C}}HO)_x-H$, where x is an integer of from 3 to 35,

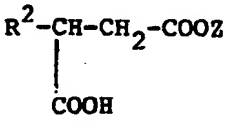
and the salts of these compounds with inorganic or organic bases, possess excellent surface active properties and good tolerance to hard water.

These compounds can also be produced by generally known methods. For example, a dicarboxylic acid anhydride of the general formula



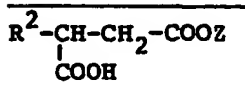
may be reacted with a polyalkyleneglycol of the general formula HOZ. The two substances may be reacted together at elevated temperature, optionally in the presence of a solvent, to produce the hemiester of general formula I.

Examples of new surface active agents according to the invention, which may be produced by the above described method, are as follows:



	R^2	Z			
1	n-nonenyl	$-(CH_2CH_2O)_{34}-H$	waxlike	30-35	17.5
2	n-dodecenyl	$-(CH_2CH_2O)_{34}-H$	"	30-35	18.0
3	nonenyl	$-(CH_2CH_2O)_9-H$	viscous	100-110	15.0
4	dodecenyl	$-(CH_2CH_2O)_9-H$	"	100-110	15.0

It was found that the acidic strength of the surface active agents of the general formula I according to the invention is influenced by the group Z, as shown below by the following examples:



R^2	Z	pH in distilled water 1.0 g/l	0.1 g/l	0.01 g/l
n-nonenyl	$-(CH_2CH_2O)_{34}-H$	3.8	4.2	4.9
n-nonenyl	$-(CH_2CH_2O)_9-H$	3.6	4.0	5.0

We have also surprisingly found that by the

appropriate variation of the group Z a whole series of surface active agents can be produced across the 3 to 6 pH range. The invention thus provides an extensive variety of hard water tolerant anionic surface active agents for many different applications.

We have also found that the new surface active agents, even at very low concentration, reduce the surface tension of water, as illustrated below:

R^2-CH(COOH)-CH_2COOZ		Surface tension in distilled water
R^2	Z	25°C, 1.0 g/l (dyn/cm)
n-nonenyl	$-(CH_2CH_2O)_{34}-H$	54.7
n-dodecenyl	$-(CH_2CH_2O)_{34}-H$	40.9

The surface active agents according to the invention can be mixed with nonionic and anionic type surfactants and thus can advantageously be used with most common emulsifying mixtures, as the anionic component.

The use of the new surfactants is particularly advisable in products in which for some reason an acidic medium must be provided, e.g. in certain plant protective chemicals which after formulation must be stored in an acidic medium to prevent decomposition.

The salts of the surfactants of the invention with inorganic and organic bases can be utilised in all fields where other anionic surface active agents are used.

The invention is illustrated by the following examples.

Example 1

22.4 g nonenyl-succinic acid anhydride is warmed up to 90°C with constant mixing. 150.0 g polyethylene glycol 1500 (x = 34) is added to it in drops over 30 minutes, then stirred for a full hour at a temperature of 90°C. Cooled down it yields the desired surface active agent. Acid no.: 31.5 mg KOH/g, HLB: 15.0.

Example 2

167 g dodecylpolyglycolether (x = 13, OH: 66-69 mg KOH/g) and 20 g succinic acid anhydride are reacted at 90°C for one hour. Cooled down to room temperature, the mixture yields the desired surface active agent. Acid no.: 59-61 mg KOH/g, HLB: 12.

Example 3

22.4 g nonenyl-succinic acid anhydride is warmed up to 90°C with constant mixing. 29.0 polyethylene glycol 300 (x = 7) is added to it in drops over 30 minutes, and the mixture is stirred for a full hour at a temperature of 90°C. Cooled down, it yields the desired surface active agent. Acid no.: 106-109 mg KOH/g, HLB: 10.5.

CLAIMS:

1. Anionic surface active agents of the general formula I

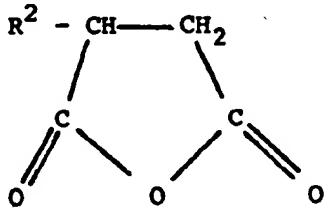
(I)

where R^2 is C_{8-12} alkyl or alkenyl; and

Z is $-(CH_2CH_2O)_xH$ or $-(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_xH$, where x is an integer of 3 to 35, and the salts thereof with inorganic or organic bases.

2. Surface active agents as claimed in claim 1 in which R^2 is nonenyl or dodecenyl.

3. A process for the preparation of a surface active agent of formula I as defined in claim 1 in which a dicarboxylic acid anhydride of the general formula



is reacted with a polyalkyleneglycol of the formula HOZ.